Equations-of-motion method including renormalization and double-excitation mixing*

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The equations-of-motion method is discussed as an approach to calculating excitation energies and transition moments directly. The proposed solution [T. Shibuya and V. McKoy, Phys. Rev. A **2**, 2208 (1970)] of these equations is extended in two ways. First we include the proper renormalization of the equations with respect to the ground state particle–hole densities. We then show how to include the effects of two-particle–hole components in excited states which are primarily single-particle–hole states. This is seen to be equivalent to a single-particle–hole theory with a normalized interaction. Applications to various diatomic and polyatomic molecules indicate that the theory can predict excitation energies and transition moments accurately and economically.

I. INTRODUCTION

The conventional approach to predicting the excitation energy of an excited state of a molecule would be to solve Schrödinger's equation separately for the energies and wavefunctions of the ground and excited state. In this way one calculates the total energies and absolute wavefunctions of two states in order to calculate the excitation energy. In spectroscopy the quantities of direct physical interest in a transition are excitation frequency and oscillator strength and not really the total energies and wavefunctions of the states. On the other hand the equations-of-motion method[1] attempts to calculate the excitation frequency of a transition directly. Observables such as the excitation energy of an excited state and its transition matrix elements involve not so much the total wavefunctions as certain relationships between them. Accordingly in the equations-of-motion method one calculates excitation operators rather than wavefunctions. An excitation operator, O_λ^+, relates one state $|\lambda\rangle$ to the ground state $|0\rangle$ through a set of amplitudes. These amplitudes and an excitation frequency are the solution of the equations of motion. In summary, the philosophy of this approach is to shift emphasis away from absolute quantities such as total energies and to concentrate on the relative quantities, e.g., excitation energies directly accessible to measurement.[1]

The main objective of the equations-of-motion method is to obtain excitation energies of excited states relative to a correlated ground state directly. Thus the excitations are out of a correlated ground state. This provides some definite advantages over an approximation in which the excited state wavefunction is correlated but the Hartree–Fock (HF) wavefunction is used for the ground state. With a correlated ground state, potential energy curves should dissociate to the correct dissociation limits. Moreover the results in this approximation satisfy the energy-weighted sum rule which for electric dipole transitions is the Thomas–Reiche–Kuhn theorem.[2] This is very useful if one is looking at various electric dipole transitions of a molecule since the predicted intensities would be distributed in a way consistent with the sum rule. Finally, Harris[3] has shown that in the time-dependent HF approximation, which is just the lowest order solution to the equations of motion with an implied correlated ground state, the different expressions for the oscillator strengths are equivalent with one another. If the dipole velocity and length forms of the oscillator strength disagree with each other in a basis set calculation, the difficulty is in the finite basis set. This result can be very useful in practical applications. Harris[3] also shows that in this approximation the two expressions for the rotational strength are also equivalent. There is no origin dependence and the rotational strength sum rule holds. These properties are necessary for a theory to have wide applicability in spectroscopy.

Recently we proposed a solution of the equations of motion which should be practical and accurate enough for describing the electronically excited states of molecules.[4] We started from Rowe's variational form of the equations of motion[1] which states that the operator O_λ^+ for creating an excited state $|\lambda\rangle$ from the ground state is exactly a solution of the equation

$$\langle 0|[\delta O_\lambda, H, O_\lambda^+]|0\rangle = \omega_\lambda \langle 0|[\delta O_\lambda, O_\lambda^+]|0\rangle, \quad (1)$$

where ω_λ is the excitation energy $(E_\lambda - E_0)$ and the double commutator is defined by

$$2[A, H, B] = [A, [H, B]] + [[A, H], B]. \quad (2)$$

The operator O_λ^+ contains a set of amplitudes determining the relative importance of various particle–hole excitations in generating the state $|\lambda\rangle$ out of $|0\rangle$, i.e.,

$$O_\lambda^+ |0\rangle = |\lambda\rangle. \quad (3)$$

We obtain these amplitudes and the excitation fre-

quency ω_λ from the solution of Eq. (1). One must assume some approximate ground state $|\phi\rangle$ to evaluate the expectation values of the commutators in Eq. (1). However, the commutators will be of lower particle rank than the operators themselves and hence their expectation values should depend on relatively simple properties of the ground state. For example, the operator $a_i^+a_mHa_n^+a_j$ is of a particle rank two greater than the operator $[a_i^+a_m, H, a_n^+a_j]$. This is a particular merit of the equations-of-motion method. If one evaluates Eq. (1) using the HF wavefunction as the approximate ground state and O_λ^+ with single-particle–hole creation and destruction operators, the resulting equations are those of the random phase approximation (RPA). For some cases this approximation leads to instabilities in Eq. (1).[5] In Ref. 4 we proposed a higher order solution to Eq. (1) in which, with the same O_λ^+ as in the RPA, the expectation values of the commutators were explicitly expanded in powers of the correlation coefficients of the ground state. These equations referred to as the higher RPA[6] gave encouraging results for the $N\rightarrow V$ and $N\rightarrow T$ transitions of ethylene.[7]

In this paper we improve the theory of Ref. 4 in two respects. First we include the proper renormalization of the equations due to the particle–hole densities of the ground state. The resulting equations now contain renormalized matrix elements and amplitudes but have the same matrix form. Second, we discuss ways of estimating the effect of two-particle–hole states on the excitation energy of an excited state. Generally the most important components of an excited state are the singly excited configurations, i.e., single-particle–hole pairs. In the complete expansion of the excitation operator O_λ^+ these would have the largest amplitudes. However, for some states doubly excited configurations (relative to the ground state) can affect the excitation energy by a few electron volts. We also illustrate how the theory including two-particle-hole states is equivalent to the single-particle–hole theory with a renormalized interaction.[8,9]

II. A SUMMARY OF VARIOUS APPROXIMATIONS

In Eq. (1) one must specify which type of excitations are to be included in the excitation operator O_λ^+ and which approximate ground state wavefunction will be used to evaluate the expectation values of the commutators. For atomic and molecular systems singly excited configurations are the most important in low-lying excited states and hence O_λ^+ contains only single-particle–hole operators ($1p$–$1h$). If we completely accept the Hartree–Fock approximation for the ground state then O_λ^+ is, in second quantized form,[10]

$$O^+(\lambda SM)=\sum_{m\gamma} Y_{m\gamma}(\lambda S)C_{m\gamma}^+(SM), \tag{4}$$

where $Y_{m\gamma}$ is the amplitude for the $m\gamma$ particle–hole pair and $C_{m\gamma}^+(SM)$ are spin-adapted creation operators defined by

$$C_{m\gamma}^+(00)=(1/\sqrt{2})\,(c_{m\alpha}^+c_{\gamma\alpha}+c_{m\beta}^+c_{\gamma\beta}), \tag{5a}$$

$$\begin{aligned} C_{m\gamma}^+(1M) &= -c_{m\alpha}^+c_{\gamma\beta}, && M=+1\\ &= (1/\sqrt{2})\,(c_{m\alpha}^+c_{\gamma\alpha}-c_{m\beta}^+c_{\gamma\beta}), && M=0\\ &= c_{m\beta}^+c_{\gamma\alpha}, && M=-1. \end{aligned} \tag{5b}$$

m specifies a particle state and γ a hole state, while α and β are the usual spin functions. The operators $c_{i\alpha}^+$ and $c_{i\alpha}$ are creation and annihilation operators for spin–orbital $i\alpha$. Note that $C_{m\gamma}^+(SM)$ creates a state with spin symmetry SM when it acts on a singlet state.

With $O^+(\lambda SM)$ of Eq. (4) and an HF state, the excitation energy of state $|\lambda\rangle$ relative to the HF energy of the ground state is given by

$$A^0(S)\,Y(\lambda S)=\omega(\lambda S)\,Y(\lambda S), \tag{6}$$

where

$$\begin{aligned} A_{m\gamma,n\delta}{}^0(S) &\equiv \langle \mathrm{HF}\,|[C_{m\gamma}(SM), H, C_{n\delta}^+(SM)]|\,\mathrm{HF}\rangle\\ &= \delta_{mn}\delta_{\gamma\delta}(\epsilon_m-\epsilon_\gamma)-V_{m\delta n\gamma}+\delta_{S,0}(2V_{m\delta\gamma n}). \end{aligned} \tag{7}$$

In Eq. (7) ϵ_i is the HF orbital eigenvalue and

$$V_{ijkl}\equiv\langle i(1)j(2)|(r_{12})^{-1}\,|\,k(1)l(2)\rangle. \tag{8}$$

Equation (6) is the usual expression for the energy from single-excitation configuration interaction (CI). In the literature of many-body physics this equation is referred to as the Tamm–Dancoff approximation (TDA).[11]

In the next approximation one simply recognizes that the HF wavefunction is not the true ground state and hence the excitation operators must include $1p$–$1h$ destruction $C_{m\gamma}$, as well as creation, $C_{m\gamma}^+$, operators. Thus

$$O^+(\lambda SM)=\sum_{m\gamma}\{Y_{m\gamma}(\lambda S)C_{m\gamma}^+(SM) - Z_{m\gamma}(\lambda S)C_{m\gamma}(\bar{S}\bar{M})\}, \tag{9}$$

where

$$C_{m\gamma}(\bar{S}\bar{M})=(-1)^{S+M}C_{m\gamma}(S-M). \tag{10}$$

If one substitutes Eq. (9) into the equation of motion and uses the HF wavefunction to evaluate the expectation values in this equation, the random phase approximation is obtained,[12]

$$\begin{bmatrix} A^0(S) & B^0(S)\\ -B^{0*}(S) & -A^{0*}(S)\end{bmatrix}\begin{bmatrix} Y(\lambda S)\\ Z(\lambda S)\end{bmatrix}=\omega(\lambda S)\begin{bmatrix} Y(\lambda S)\\ Z(\lambda S)\end{bmatrix}, \tag{11}$$

where the elements of A^0 are defined in Eq. (7) and

$$B_{m\gamma,n\delta}{}^0(S) = -\langle \mathrm{HF}\,|[C_{m\gamma}(SM), H, C_{n\delta}(\bar{S}\bar{M})]|\,\mathrm{HF}\rangle$$
$$= -(-1)^S V_{mn\delta\gamma} + \delta_{S,0}(2V_{mn\gamma\delta}). \quad (12)$$

Since $|\,0\rangle$ is the lowest state of the Hamiltonian, one should require

$$O_\lambda\,|\,0\rangle = 0 \qquad \text{all } \lambda. \quad (13)$$

But in deriving the equations of the RPA, Eq. (11), we use the HF wavefunction to evaluate the expectation values of Eq. (1). The HF wavefunction does not satisfy Eq. (13) with the $O_\lambda{}^+$ of Eq. (9). It is well known that such inconsistency may be acceptable because the equations of motion are comparatively insensitive to the approximate ground state used to set them up.[1] It is for this reason that one does not have to be very concerned about the rigorous requirement that the $|\,0\rangle$ used to set up the equations of motion should also satisfy Eq. (13). This also applies to the higher order approximations we will derive below. One should, of course, check the consistency of this assumption. It is obvious that this assumption is weakest[7] for atomic and molecular calculations using minimum basis sets but improves in large basis set calculations with the increasing density of particle–hole pairs. The approximation should also be good for large numbers of particles.

To remove this inconsistency of the RPA we could use a correlated ground state wavefunction to set up the equations of motion. This leads to our next approximation.[4] The expectation values of Eq. (1) will now explicitly depend on the correlation coefficients. Exactly how these coefficients are determined is not very crucial. To a good approximation we can write the ground state wavefunction for a closed shell system as

$$|\,0\rangle \simeq N_0(1+U+\cdots)\,|\,\mathrm{HF}\rangle, \quad (14)$$

where N_0 is the normalization constant and

$$U = \sum_{mn,\gamma\delta}[K_{m\gamma,n\delta}c_{m\alpha}{}^+c_{n\beta}{}^+c_{\delta\beta}c_{\gamma\alpha} + \tfrac{1}{2}(K_{m\gamma,n\delta} - K_{m\delta,n\gamma})$$
$$\times \tfrac{1}{2}(c_{m\alpha}{}^+c_{n\alpha}{}^+c_{\delta\alpha}c_{\gamma\alpha} + c_{m\beta}{}^+c_{n\beta}{}^+c_{\delta\beta}c_{\gamma\beta})]. \quad (15)$$

To set up a self-consistent theory we can require that the $|\,0\rangle$ of Eq. (14) satisfy Eq. (13), which gives

$$Z_{m\gamma}(\lambda S) \simeq \sum_{n\delta} C_{m\gamma,n\delta}{}^*(S)\,Y_{n\delta}(\lambda S), \quad (16)$$

where

$$C_{m\gamma,n\delta}(S) = K_{m\gamma,n\delta} + (-1)^S(K_{m\gamma,n\delta} - K_{m\delta,n\gamma}). \quad (17)$$

We can solve these equations and the equations of motion iteratively. With the wavefunction of Eq. (14) and omitting all terms quadratic and higher in the correlation coefficients, Eq. (1) becomes[4]

$$\begin{bmatrix} A(S) & B(S) \\ -B^*(S) & -A^*(S) \end{bmatrix}\begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = \omega(\lambda S)\begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix}, \quad (18)$$

where the matrix elements of A and B are

$$A_{m\gamma,n\delta}(S) = A_{m\gamma,n\delta}{}^0(S) + \delta_{\gamma\delta}T_{mn} - \delta_{mn}T_{\gamma\delta},$$
$$B_{m\gamma,n\delta}(S) = B_{m\gamma,n\delta}{}^0(S) + (-1)^S S_{m\gamma,n\delta} + X_{m\gamma,n\delta}(S), \quad (19)$$

and

$$S_{m\gamma,n\delta} = -\sum_{p\mu}[V_{m\mu\delta p}C_{p\mu,n\gamma}(0) + V_{n\mu\gamma p}C_{p\mu,m\delta}(0)],$$
$$T_{mn} = -\tfrac{1}{2}\sum_{q\mu\nu}[V_{mq\mu\nu}C_{n\mu,q\nu}{}^*(0) + V_{\mu\nu nq}C_{m\mu,q\nu}(0)],$$
$$T_{\gamma\delta} = \tfrac{1}{2}\sum_{pq\nu}[V_{pq\gamma\nu}C_{p\delta,q\nu}{}^*(0) + V_{\delta\nu pq}C_{p\gamma,q\nu}(0)],$$
$$X_{m\gamma,n\delta}(S) = \sum_{\mu\nu} V_{\mu\nu\gamma\delta}C_{m\mu,n\nu}(S) + \sum_{pq} V_{mnpq}C_{p\gamma,q\delta}(S)$$
$$- \sum_{p\mu}[V_{m\mu p\delta}C_{p\gamma,n\mu}(S) + V_{n\mu p\gamma}C_{p\delta,m\mu}(S)]. \quad (20)$$

In Eq. (20) m, n, p, q, refer to particle states, and γ, δ, μ, ν to hole states. Equations (16) and (18) are the higher RPA.[4] For practical purposes one need not necessarily solve these equations self-consistently but could simply estimate the correlation coefficients by perturbation theory and substitute these into Eq. (20). Usually iteration does not change the excitation frequency by more than a few percent. This is expected since the equations are designed to be as insensitive as possible to the approximations made for the ground state. For molecular calculations with small basis sets the terms linear in the correlation coefficients in Eq. (20) are quite important.[7] Extensive calculations on the excited states of N_2 and CO also illustrate this.[13]

III. RENORMALIZATION OF THE EQUATIONS

We now show that we can obtain a more consistent set of equations than Eqs. (18)–(20) by including second-order density terms in the matrix elements $A_{m\gamma,n\delta}(S)$. With these additional terms we can write the equations exactly as in Eq. (18) but now with renormalized interaction matrix elements and amplitudes.

The most general equation one obtains from Eq. (1) with the $1p$–$1h$ form of $O_\lambda{}^+$, Eq. (9), is

$$\begin{bmatrix} \mathfrak{A}(S) & \mathfrak{B}(S) \\ -\mathfrak{B}^*(S) & -\mathfrak{A}^*(S) \end{bmatrix}\begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = \omega(\lambda S)\begin{bmatrix} \mathfrak{D} & 0 \\ 0 & \mathfrak{D}^* \end{bmatrix}\begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix}, \quad (21)$$

where the matrix element of $\mathfrak{A}$, $\mathfrak{B}$, and $\mathfrak{D}$ are

$$\mathfrak{A}_{m\gamma,n\delta}(S)\equiv\langle 0\,|[C_{m\gamma}(SM),H,C_{n\delta}{}^{+}(SM)]|\,0\rangle,$$

$$\mathfrak{B}_{m\gamma,n\delta}(S)\equiv-\langle 0\,|[C_{m\gamma}(SM),H,C_{n\delta}(\bar{S}\bar{M})]|\,0\rangle,$$

$$\mathfrak{D}_{m\gamma,n\delta}(S)\equiv\langle 0\,|[C_{m\gamma}(SM),C_{n\delta}{}^{+}(SM)]|\,0\rangle. \qquad (21')$$

In deriving the equations of the higher RPA we retained all terms linear in the correlation coefficients. These include the dominant corrections but it would be more complete to include terms in matrix elements, Eq. (21'), consistent with a given order in perturbation theory, e.g., VC and $(\epsilon_i-\epsilon_j)C^2$ are of the same order where V is an interaction matrix element and C a correlation coefficient. To second-order terms we can write

$$\mathfrak{A}_{m\gamma,n\delta}(S)=A_{m\gamma,n\delta}{}^{0}(S)+\delta_{\gamma\delta}[T_{mn}-\tfrac{1}{2}(\epsilon_m+\epsilon_n-2\epsilon_\gamma)\rho_{mn}{}^{(2)}]$$
$$-\delta_{mn}[T_{\gamma\delta}-\tfrac{1}{2}(2\epsilon_m-\epsilon_\gamma-\epsilon_\delta)\rho_{\gamma\delta}{}^{(2)}],$$

$$\mathfrak{B}_{m\gamma,n\delta}(S)=B_{m\gamma,n\delta}(S),$$

$$\mathfrak{D}_{m\gamma,n\delta}(S)=\delta_{mn}\delta_{\gamma\delta}+\delta_{mn}\rho_{\gamma\delta}{}^{(2)}-\delta_{\gamma\delta}\rho_{mn}{}^{(2)}. \qquad (22)$$

In Eqs. (22) A^0 is given by Eq. (7), B by Eq. (19), and T's by Eq. (20). The $\rho^{(2)}$'s are quadratic in correlation coefficients,[4]

$$\rho_{mn}{}^{(2)}=\tfrac{1}{2}\sum_{p\mu\nu}\sum_{S=0,1}C_{p\mu,m\nu}{}'(S)C_{p\mu,n\nu}{}^{*}(S),$$

$$\rho_{\gamma\delta}{}^{(2)}=-\tfrac{1}{2}\sum_{pq\mu}\sum_{S=0,1}C_{p,\mu q\gamma}{}'(S)C_{p\mu,q\delta}{}^{*}(S), \qquad (23)$$

where the C's are defined in Eq. (17) and

$$C_{m\gamma,n\delta}{}'(S)=K_{m\gamma,n\delta}+(-1)^{S}\tfrac{1}{2}(K_{m\gamma,n\delta}-K_{m\delta,n\gamma}). \qquad (24)$$

To derive Eqs. (22) we use the results

$$N_o{}^{2}\simeq 1-\langle HF\mid U^{+}U\mid HF\rangle,$$

$$\langle HF\mid U^{+}U\mid HF\rangle=-\sum_{\gamma}\rho_{\gamma\gamma}{}^{(2)}=\sum_{m}\rho_{mm}{}^{(2)}. \qquad (25)$$

Note that the ground state correlation energy is

$$E_{\text{corr}}=2\sum_{\gamma}T_{\gamma\gamma}+2(\sum_{\gamma}\epsilon_\gamma\rho_{\gamma\gamma}{}^{(2)}+\sum_{m}\epsilon_m\rho_{mm}{}^{(2)})$$
$$=-2\sum_{m}T_{mm}+2(\sum_{\gamma}\epsilon_\gamma\rho_{\gamma\gamma}{}^{(2)}+\sum_{m}\epsilon_m\rho_{mm}{}^{(2)}), \qquad (26)$$

which is just $E^{(2)}$ if the correlation coefficients of Rayleigh–Schrödinger perturbation theory are used to evaluate the T's and $\rho^{(2)}$'s leading to

$$E_{\text{corr}}=\sum_{\gamma}T_{\gamma\gamma}=-\sum_{m}T_{mm}. \qquad (26')$$

The correction term of $\mathfrak{A}$ in Eq. (22) is typically about half of that of A in Eq. (19). We will see, however, that the effect of this change in the elements of $\mathfrak{A}$ on the excitation frequencies is partly compensated for by renormalization terms in $\mathfrak{D}$. The over-all effect is usually less than 5% for the cases we have studied.[13] To a good approximation we can write

$$\mathfrak{D}_{m\gamma,n\delta}=\delta_{mn}\delta_{\gamma\delta}\,(1+\rho_{\gamma\gamma}{}^{(2)}-\rho_{mm}{}^{(2)}). \qquad (27)$$

With this diagonal form for $\mathfrak{D}$ Eq. (21) becomes

$$\begin{bmatrix}\bar{\mathfrak{A}}(S) & \bar{\mathfrak{B}}(S)\\ -\bar{\mathfrak{B}}^{*}(S) & -\bar{\mathfrak{A}}^{*}(S)\end{bmatrix}\begin{bmatrix}\bar{Y}(\lambda S)\\ Z(\bar{\lambda}S)\end{bmatrix}=\omega(\lambda S)\begin{bmatrix}\bar{Y}(\lambda S)\\ \bar{Z}(\lambda S)\end{bmatrix}, \qquad (28)$$

where the elements of $\bar{\mathfrak{A}}$, $\bar{\mathfrak{B}}$, $\bar{Y}$, and $\bar{Z}$ have the renormalized forms

$$\bar{\mathfrak{A}}_{m\gamma,n\delta}(S)=f_{m\gamma}{}^{-1}\mathfrak{A}_{m\gamma,n\delta}(S)f_{n\delta}{}^{-1},$$

$$\bar{\mathfrak{B}}_{m\gamma,n\delta}(S)=f_{m\gamma}{}^{-1}\mathfrak{B}_{m\gamma,n\delta}(S)f_{n\delta}{}^{-1},$$

$$\bar{Y}_{m\gamma}(\lambda S)=f_{m\gamma}Y_{m\gamma}(\lambda S),$$

$$\bar{Z}_{m\gamma}(\lambda S)=f_{m\gamma}Z_{m\gamma}(\lambda S), \qquad (28')$$

with the renormalization factor

$$f_{m\gamma}=(1+\rho_{\gamma\gamma}{}^{(2)}-\rho_{mm}{}^{(2)})^{1/2}. \qquad (29)$$

A major advantage of the approximate expression equation (28) is that the matrices $\bar{\mathfrak{A}}$ and $\bar{\mathfrak{B}}$ remain symmetrical and the equations have the same form as the RPA.

The orthogonality condition implies that the amplitudes satisfy

$$Y^{\dagger}(\lambda' S)\mathfrak{D}Y(\lambda S)-Z^{\dagger}(\lambda' S)\mathfrak{D}^{*}Z(\lambda S)=\delta_{\lambda'\lambda} \qquad (30)$$

or, in terms of $\bar{Y}$ and $\bar{Z}$,

$$\bar{Y}^{\dagger}(\lambda' S)\,\bar{Y}(\lambda S)-\bar{Z}^{\dagger}(\lambda' S)\bar{Z}(\lambda S)=\delta_{\lambda'\lambda}, \qquad (31)$$

which again has the same form as in all the other approximations.

IV. COUPLING OF DOUBLE EXCITATIONS

The low-lying excited states of molecular systems are primarily one-electron excitations relative to the ground state. These are single-particle–hole ($1p$–$1h$) states and hence the excitation operator $O_\lambda{}^{+}$, Eq. (9), contains just $1p$–$1h$ creation and destruction operators. An excited state also contains two- and more-particle–hole components corresponding to two, three, etc., electron excitations out of the ground state. The amplitudes, $Y_{m\gamma,n\delta}{}^{(2)}$ and $Z_{m\gamma,n\delta}{}^{(2)}$, of these components of $O_\lambda{}^{+}$, will be much smaller than those of the $1p$–$1h$

TABLE I. The $2p$–$2h$ creation operators $\Gamma^{+}_{m\gamma,n\delta}$.

$S=M=0$[a]

$$\Gamma^{+}_{m\gamma,m\gamma}=c_{m\alpha}{}^{+}c_{m\beta}{}^{+}c_{\gamma\beta}c_{\gamma\alpha}=C_{m\gamma}{}^{+}(00)\,C_{m\gamma}{}^{+}(00)$$

$$\Gamma^{+}_{m\gamma,n\gamma}=(1/\sqrt{2})\,[c_{m\alpha}{}^{+}c_{n\beta}{}^{+}+c_{n\alpha}{}^{+}c_{m\beta}{}^{+}]c_{\gamma\beta}c_{\gamma\alpha}=\sqrt{2}C_{m\gamma}{}^{+}(00)\,C_{n\gamma}{}^{+}(00)\qquad(m\neq n)$$

$$\Gamma^{+}_{m\gamma,m\delta}=(1/\sqrt{2})\,c_{m\alpha}{}^{+}c_{m\beta}{}^{+}[c_{\delta\beta}c_{\gamma\alpha}+c_{\gamma\beta}c_{\delta\alpha}]=\sqrt{2}C_{m\gamma}{}^{+}(00)\,C_{m\delta}{}^{+}(00)\qquad(\gamma\neq\delta)$$

$$\Gamma^{+}_{(m\gamma,n\delta)_1}=\tfrac{1}{2}[c_{m\alpha}{}^{+}c_{n\beta}{}^{+}+c_{n\alpha}{}^{+}c_{m\beta}{}^{+}][c_{\delta\beta}c_{\gamma\alpha}+c_{\gamma\beta}c_{\delta\alpha}]\qquad(m\neq n,\ \gamma\neq\delta)$$

$$=\tfrac{1}{2}[C_{m\gamma}{}^{+}(00)\,C_{n\delta}{}^{+}(00)+C_{m\delta}{}^{+}(00)\,C_{n\gamma}{}^{+}(00)]$$

$$\Gamma^{+}_{(m\gamma,n\delta)_2}=(1/\sqrt{3})\,\{[c_{m\alpha}{}^{+}c_{n\alpha}{}^{+}c_{\delta\alpha}c_{\gamma\alpha}+c_{m\beta}{}^{+}c_{n\beta}{}^{+}c_{\delta\beta}c_{\gamma\beta}]+\tfrac{1}{2}[c_{m\alpha}{}^{+}c_{n\beta}{}^{+}-c_{n\alpha}{}^{+}c_{m\beta}{}^{+}][c_{\delta\beta}c_{\gamma\alpha}-c_{\gamma\beta}c_{\delta\alpha}]\}\qquad(m\neq n,\ \gamma\neq\delta)$$

$$=(1/\sqrt{3})\,[C_{m\gamma}{}^{+}(00)\,C_{n\delta}{}^{+}(00)-C_{m\delta}{}^{+}(00)\,C_{n\gamma}{}^{+}(00)]$$

$S=1,\ M=0$[b]

$$\Gamma^{+}_{(m\gamma,n\gamma)_1}=(1/\sqrt{2})\,[c_{m\alpha}{}^{+}c_{n\beta}{}^{+}-c_{n\alpha}{}^{+}c_{m\beta}{}^{+}]c_{\gamma\beta}c_{\gamma\alpha}\qquad(m\neq n)$$

$$=(1/\sqrt{2})\,[C_{m\gamma}{}^{+}(10)\,C_{n\gamma}{}^{+}(00)-C_{n\gamma}{}^{+}(10)\,C_{m\gamma}{}^{+}(00)]$$

$$\Gamma^{+}_{(m\gamma,n\delta)_1}=\tfrac{1}{2}[c_{m\alpha}{}^{+}c_{n\beta}{}^{+}-c_{n\alpha}{}^{+}c_{m\beta}{}^{+}][c_{\delta\beta}c_{\gamma\alpha}+c_{\gamma\beta}c_{\delta\alpha}]\qquad(m\neq n,\ \gamma\neq\delta)$$

$$=\tfrac{1}{2}[C_{m\gamma}{}^{+}(10)\,C_{n\delta}{}^{+}(00)-C_{n\delta}{}^{+}(10)\,C_{m\gamma}{}^{+}(00)+C_{m\delta}{}^{+}(10)\,C_{n\gamma}{}^{+}(00)-C_{n\gamma}{}^{+}(10)\,C_{m\delta}{}^{+}(00)]$$

$$\Gamma^{+}_{(m\gamma,m\delta)_2}=(1/\sqrt{2})\,c_{m\alpha}{}^{+}c_{m\beta}{}^{+}[c_{\delta\beta}c_{\gamma\alpha}-c_{\gamma\beta}c_{\delta\alpha}]\qquad(\gamma\neq\delta)$$

$$=(1/\sqrt{2})\,[C_{m\gamma}{}^{+}(10)\,C_{m\delta}{}^{+}(00)-C_{m\delta}{}^{+}(10)\,C_{m\gamma}{}^{+}(00)]$$

$$\Gamma^{+}_{(m\gamma,n\delta)_2}=\tfrac{1}{2}[c_{m\alpha}{}^{+}c_{n\beta}{}^{+}+c_{n\alpha}{}^{+}c_{m\beta}{}^{+}][c_{\delta\beta}c_{\gamma\alpha}-c_{\gamma\beta}c_{\delta\alpha}]\qquad(m\neq n,\ \gamma\neq\delta)$$

$$=\tfrac{1}{2}[C_{m\gamma}{}^{+}(10)\,C_{n\delta}{}^{+}(00)-C_{n\delta}{}^{+}(10)\,C_{m\gamma}{}^{+}(00)-C_{m\delta}{}^{+}(10)\,C_{n\gamma}{}^{+}(00)+C_{n\gamma}{}^{+}(10)\,C_{m\delta}{}^{+}(00)]$$

$$\Gamma^{+}_{(m\gamma,n\delta)_3}=(1/\sqrt{2})\,[c_{m\alpha}{}^{+}c_{n\alpha}{}^{+}c_{\delta\alpha}c_{\gamma\alpha}-c_{m\beta}{}^{+}c_{n\beta}{}^{+}c_{\delta\beta}c_{\gamma\beta}]\qquad(m\neq n,\ \gamma\neq\delta)$$

$$=(1/\sqrt{2})\,[C_{m\gamma}{}^{+}(10)\,C_{n\delta}{}^{+}(00)+C_{n\delta}{}^{+}(10)\,C_{m\gamma}{}^{+}(00)]$$

[a] The subscripts on the indices for Γ^{+} indicate different spin couplings of the four orbitals, m, γ, n, and δ; there are two independent singlet excited states if $m\neq n$ and $\gamma\neq\delta$. Formal development of the equations of Sec. IV up to and including (44) does not specify these subscripts explicitly, but in fact indices describing $2p$–$2h$ excitations must include them. Starting from Eq. (45), interaction terms in $A^{0(2,2)}$ are ignored. Thus the two singlet spin couplings are degenerate, and since they are also chosen here to be orthogonal (diagonalizing the full $D^{0(2,2)}$ matrix) they can be combined into a single effective state for the index $(m\gamma, n\delta)$.

[b] These operators diagonalize $D^{0(2,2)}$ of Eq. (45). The subscripts on the indices $(m\gamma, n\delta)$ indicate the three possible independent spin couplings for the $2p$–$2h$ state when $m\neq n$ and $\gamma\neq\delta$. See Footnote a.

components but their effect on large excitation energies, e.g., 8–12 eV, can be significant.[13] Their effect on transition moments will be very small. In this section we show how these $2p$–$2h$ states should be rigorously included in the theory. An important conclusion is that the theory with both $1p$–$1h$ and $2p$–$2h$ states can be shown to be equivalent to the $1p$–$1h$ theory with a renormalized interaction.[14] Finally we derive a simple and practical approximation for including the effects of these double excitations.

To include the effect of double excitations we add $2p$–$2h$ creation and destruction operators,

$$\sum_{m\gamma n\delta}[Y_{m\gamma,n\delta}{}^{(2)}(\lambda S)\,\Gamma^{+}_{m\gamma,n\delta}(SM)-Z_{m\gamma,n\delta}{}^{(2)}(\lambda S)\,\Gamma_{m\gamma,n\delta}(\bar{S}\bar{M})],\quad(32)$$

to the $O_\lambda{}^{+}$ of Eq. (9). Here $\Gamma^{+}_{m\gamma,n\delta}$ is a $2p$–$2h$ creation operator and $Y^{(2)}$ and $Z^{(2)}$ are amplitudes to be determined. The explicit expressions for Γ^{+} are shown in Table I. Substitution of $O_\lambda{}^{+}$ containing the terms in Eq. (32) into the variational form of the equations of motion, Eq. (1) gives

$$\begin{bmatrix}\mathcal{A} & \mathcal{B}\\ -\mathcal{B}^{*} & -\mathcal{A}^{*}\end{bmatrix}\begin{bmatrix}Y\\ Z\end{bmatrix}+\begin{bmatrix}\mathcal{A}^{(1,2)} & \mathcal{B}^{(1,2)}\\ -\mathcal{B}^{(1,2)*} & -\mathcal{A}^{(1,2)*}\end{bmatrix}\begin{bmatrix}Y^{(2)}\\ Z^{(2)}\end{bmatrix}=\omega\begin{bmatrix}\mathfrak{D} & 0\\ 0 & \mathfrak{D}^{*}\end{bmatrix}\begin{bmatrix}Y\\ Z\end{bmatrix},\qquad(33a)$$

and

$$\begin{bmatrix} \tilde{\mathfrak{A}}^{(1,2)*} & \tilde{\mathfrak{B}}^{(1,2)} \\ -\tilde{\mathfrak{B}}^{(1,2)*} & \tilde{\mathfrak{A}}^{(1,2)} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} + \begin{bmatrix} \mathfrak{A}^{(2,2)} & \mathfrak{B}^{(2,2)} \\ -\mathfrak{B}^{(2,2)*} & -\mathfrak{A}^{(2,2)*} \end{bmatrix} \begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} = \omega \begin{bmatrix} \mathfrak{D}^{(2,2)} & 0 \\ 0 & \mathfrak{D}^{(2,2)*} \end{bmatrix} \begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix}. \tag{33b}$$

The dimensionality of the equations is determined by the number of $1p$–$1h$ and $2p$–$2h$ amplitudes included in the summations of Eqs. (9) and (32). In Eqs. (33), the matrix elements of $\mathfrak{A}$ and $\mathfrak{B}$ are given in Eqs. (21′), and the elements of $\mathfrak{A}^{(1,2)}$, $\mathfrak{B}^{(1,2)}$, $\mathfrak{A}^{(2,2)}$, $\mathfrak{B}^{(2,2)}$ are defined by

$$\mathfrak{A}_{m'\gamma';m\gamma,n\delta}{}^{(1,2)}(S) \equiv \langle 0 \,|[C_{m'\gamma'}(SM), H, \Gamma^{+}{}_{m\gamma,n\delta}(SM)]|\, 0\rangle, \tag{34a}$$

$$\mathfrak{B}_{m'\gamma';m\gamma,n\delta}{}^{(1,2)}(S) \equiv -\langle 0 \,|[C_{m'\gamma'}(SM), H, \Gamma_{m\gamma,n\delta}(\bar{S}\bar{M})]|\, 0\rangle, \tag{34b}$$

$$\mathfrak{A}_{m'\gamma',n'\delta';m\gamma,n\delta}{}^{(2,2)}(S) \equiv \langle 0 \,|[\Gamma_{m'\gamma',n'\delta'}(SM), H, \Gamma^{+}{}_{m\gamma,n\delta}(SM)]|\, 0\rangle, \tag{35a}$$

$$\mathfrak{B}_{m'\gamma',n'\delta';m\gamma,n\delta}{}^{(2,2)}(S) \equiv -\langle 0 \,|[\Gamma_{m'\gamma',n'\delta'}(SM), H, \Gamma_{m\gamma,n\delta}(\bar{S}\bar{M})]|\, 0\rangle, \tag{35b}$$

$$\mathfrak{D}_{m'\gamma',n'\delta';m\gamma,n\delta}{}^{(2,2)}(S) \equiv \langle 0 \,|[\Gamma_{m'\gamma',n'\delta'}(SM), \Gamma^{+}{}_{m\gamma,n\delta}(SM)]|\, 0\rangle. \tag{36}$$

In Eqs. (33) we have dropped the state label S for convenience.

We now show how Eqs. (33) containing both $1p$–$1h$ and $2p$–$2h$ amplitudes are equivalent to a $1p$–$1h$ theory with a renormalized interaction. Hence to include the effect of double excitations on excitation energies we can renormalize the single excitation theory. It is obviously very important to recognize this in interpreting semiempirical calculations. First, we note that the solution of Eq. (33b) for $Y^{(2)}$ and $Z^{(2)}$ involves the inverse of the matrix

$$\begin{bmatrix} \{\mathfrak{A}^{(2,2)}-\omega\mathfrak{D}^{(2,2)}\} & \mathfrak{B}^{(2,2)} \\ -\mathfrak{B}^{(2,2)*} & -\{\mathfrak{A}^{(2,2)}+\omega\mathfrak{D}^{(2,2)}\}^{*} \end{bmatrix}. \tag{37a}$$

The inverse of the matrix Eq. (37a) has the form

$$\begin{bmatrix} \alpha & \beta \\ -\tilde{\beta}^{*} & -\delta^{*} \end{bmatrix} \tag{37b}$$

with the properties

$$\tilde{\alpha}=\alpha^{*}; \qquad \tilde{\delta}=\delta^{*}. \tag{37c}$$

The submatrices α, β, δ have the same dimensions as $\mathfrak{A}^{(2,2)}$. We can now write

$$\begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} = -\begin{bmatrix} \alpha & \beta \\ -\tilde{\beta}^{*} & \delta^{*} \end{bmatrix} \begin{bmatrix} \tilde{a}^{*} & \tilde{b} \\ -\tilde{b}^{*} & -\tilde{a} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix}, \tag{38}$$

where $a \equiv \mathfrak{A}^{(1,2)}$; $b \equiv \mathfrak{B}^{(1,2)}$. With Eq. (38) the second term on the left-hand side of Eq. (33a) becomes

$$\begin{bmatrix} a & b \\ -b^{*} & -a^{*} \end{bmatrix} \begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} = -\begin{bmatrix} \Delta_a & \Delta_b \\ -\tilde{\Delta}_b{}^{*} & -\Delta_a{}^{*} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix}, \tag{39}$$

where

$$\begin{aligned} \Delta_a &= a\alpha\tilde{a}^{*} + b\delta^{*}\tilde{b}^{*} - (a\beta\tilde{b}^{*} + b\tilde{\beta}^{*}\tilde{a}^{*}), \\ \Delta_d &= a\delta\tilde{a}^{*} + b\alpha^{*}\tilde{b}^{*} - (a\tilde{\beta}\tilde{b}^{*} + b\beta^{*}\tilde{a}^{*}), \\ \Delta_b &= a\alpha\tilde{b} + b\delta^{*}\tilde{a} - (a\beta\tilde{a} + b\tilde{\beta}^{*}\tilde{b}). \end{aligned} \tag{40}$$

Equation (33a) now reduces to an eigenvalue problem in the $1p$–$1h$ amplitudes only:

$$\begin{bmatrix} \mathfrak{A}_1 & \mathfrak{B} \\ -\mathfrak{B}^{*} & -\mathfrak{A}_2{}^{*} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} = \omega \begin{bmatrix} \mathfrak{D} & 0 \\ 0 & \mathfrak{D}^{*} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix}, \tag{41}$$

with

$$\begin{aligned} \mathfrak{A}_1 &= \mathfrak{A} - \Delta_a, \\ \mathfrak{A}_2 &= \mathfrak{A} - \Delta_d, \\ \mathfrak{B} &= \mathfrak{B} - \Delta_b, \\ \mathfrak{D} &= \mathfrak{D}. \end{aligned} \tag{42}$$

Note that α, β, and δ are functions of ω and hence so are $\mathfrak{A}_1$, $\mathfrak{A}_2$, and $\mathfrak{B}$. In the $1p$–$1h$ approximation only the matrices $\mathfrak{A}$ and $\mathfrak{B}$ would appear in Eq. (41). The inclusion of $2p$–$2h$ excitations leads to a renormalized interaction implied in Eq. (42).

Since the effects due to $2p$–$2h$ components are expected to be small we can replace $|\,0\rangle$ by $|\,HF\rangle$ in evaluating the matrix elements $\mathfrak{A}^{(1,2)}$ etc., Eqs. (34)–(36). In this approximation $\mathfrak{B}^{0(1,2)}$ and $\mathfrak{B}^{0(2,2)}$ vanish and

$$\begin{aligned} \alpha &= (A^{0(2,2)} - \omega D^{0(2,2)})^{-1}, \\ \delta^{*} &= (A^{0(2,2)*} + \omega D^{0(2,2)*})^{-1}, \\ \beta &= 0. \end{aligned} \tag{43}$$

TABLE II. Matrix elements of $A^{0(1,2)}$.

$S=0$[a]

$$A^{0(1,2)}{}_{m'\gamma';m\gamma,m\gamma}=\sqrt{2}\,(\delta_{\gamma'\gamma}V_{\gamma m'mm}-\delta_{m'm}V_{\gamma\gamma m\gamma'})$$

$$A^{0(1,2)}{}_{m'\gamma';m\gamma,n\gamma}=\delta_{\gamma'\gamma}(V_{\gamma m'mn}+V_{\gamma m'nm})-\delta_{m'm}V_{\gamma\gamma n\gamma'}-\delta_{m'n}V_{\gamma\gamma m\gamma'} \qquad (m\neq n)$$

$$A^{0(1,2)}{}_{m'\gamma';m\gamma,m\delta}=\delta_{\gamma'\gamma}V_{\delta m'mm}+\delta_{\gamma'\delta}V_{\gamma m'mm}-\delta_{m'm}(V_{\gamma\delta m\gamma'}+V_{\delta\gamma m\gamma'}) \qquad (\gamma\neq\delta)$$

$$A^{0(1,2)}{}_{m'\gamma';(m\gamma,n\delta)_1}=(1/\sqrt{2})\,\{\delta_{\gamma'\gamma}(V_{\delta m'mn}+V_{\delta m'nm})+\delta_{\gamma'\delta}(V_{\gamma m'mn}+V_{\gamma m'nm})$$
$$-\delta_{m'm}(V_{\gamma\delta n\gamma'}+V_{\delta\gamma n\gamma'})-\delta_{m'n}(V_{\gamma\delta m\gamma'}+V_{\delta\gamma m\gamma'})\} \qquad (m\neq n,\ \gamma\neq\delta)$$

$$A^{0(1,2)}{}_{m'\gamma';(m\gamma,n\delta)_2}=(\tfrac{3}{2})^{1/2}\{\delta_{\gamma'\delta}(V_{\gamma m'mn}-V_{\gamma m'nm})-\delta_{\gamma'\gamma}(V_{\delta m'mn}-V_{\delta m'nm})+\delta_{m'm}(V_{\gamma\delta n\gamma'}-V_{\delta\gamma n\gamma'})-\delta_{m'n}(V_{\gamma\delta m\gamma'}-V_{\delta\gamma m\gamma'}) \qquad (m\neq n,\ \gamma\neq\delta)$$

$S=1$[b]

$$A^{0(1,2)}{}_{m'\gamma';(m\gamma,n\gamma)_1}=-\delta_{\gamma'\gamma}(V_{\gamma m'mn}-V_{\gamma m'nm})-\delta_{m'm}V_{\gamma\gamma n\gamma'}+\delta_{m'n}V_{\gamma\gamma m\gamma'} \qquad (m\neq n)$$

$$A^{0(1,2)}{}_{m'\gamma';(m\gamma,n\delta)_1}=(1/\sqrt{2})\,\{-\delta_{\gamma'\gamma}(V_{\delta m'mn}-V_{\delta m'nm})-\delta_{\gamma'\delta}(V_{\gamma m'mn}-V_{\gamma m'nm})$$
$$-\delta_{m'm}(V_{\gamma\delta n\gamma'}+V_{\delta\gamma n\gamma'})+\delta_{m'n}(V_{\gamma\delta m\gamma'}+V_{\delta\gamma m\gamma'})\} \qquad (m\neq n,\ n\neq\delta)$$

$$A^{0(1,2)}{}_{m'\gamma';(m\gamma,m\delta)_2}=\delta_{\gamma'\gamma}V_{\delta m'mm}-\delta_{\gamma'\delta}V_{\gamma m'mm}+\delta_{m'm}(V_{\gamma\delta m\gamma'}-V_{\delta\gamma m\gamma'}) \qquad (\gamma\neq\delta)$$

$$A^{0(1,2)}{}_{m'\gamma';(m\gamma,n\delta)_2}=(1/\sqrt{2})\,\{\delta_{\gamma'\gamma}(V_{\delta m'mn}+V_{\delta m'nm})-\delta_{\gamma'\delta}(V_{\gamma m'mn}+V_{\delta m'nm})+\delta_{m'm}(V_{\gamma\delta n\gamma'}-V_{\delta\gamma n\gamma'})+\delta_{m'n}(V_{\gamma\delta m\gamma'}-V_{\delta\gamma m\gamma'})\} \qquad (m\neq n,\ \gamma\neq\delta)$$

$$A^{0(1,2)}{}_{m'\gamma';(m\gamma,n\delta)_3}=-\delta_{\gamma\gamma'}(V_{\delta m'mn}-V_{\delta m'nm})+\delta_{\gamma'\delta}(V_{\gamma m'mn}-V_{\gamma m'nm})+\delta_{m'm}(V_{\gamma\delta n\gamma'}-V_{\delta\gamma n\gamma'})-\delta_{m'n}(V_{\gamma\delta m\gamma'}-V_{\delta\gamma m\gamma'}) \qquad (m\neq n,\ \gamma\neq\delta)$$

[a] These elements should be used in Eq. (46).
[b] These elements should be used in Eq. (47).

With Eq. (43) Eqs. (40) become

$$\Delta_a=A^{0(1,2)}\alpha\tilde{A}^{0(1,2)*},$$
$$\Delta_d=A^{0(1,2)}\delta\tilde{A}^{0(1,2)*},$$
$$\Delta_b=0. \qquad (44)$$

If we further ignore the interaction terms in $A^{0(2,2)}$ it follows that:

$$A_{m'\gamma',n'\delta';m\gamma,n\delta}{}^{0(2,2)}(S)=(\epsilon_m+\epsilon_n-\epsilon_\gamma-\epsilon_\delta)D_{m'\gamma',n'\delta';m\gamma,n\delta}{}^{0(2,2)}. \qquad (45)$$

We can make the matrix $D^{0(2,2)}$ diagonal by choosing the $2p$–$2h$ creation operators Γ^+ of Table I. The matrix elements of $A^{0(1,2)}$ in this basis are shown in Table II. With these elements we have

$$\{\Delta_a(\lambda 0)\}_{m'\gamma',n'\delta'}=\sum_{m\gamma}\frac{A_{m'\gamma';m\gamma,m\gamma}{}^{0(1,2)}A_{n'\delta';m\gamma,m\gamma}{}^{0(1,2)*}}{2(\epsilon_m-\epsilon_\gamma)-\omega(\lambda 0)}+\sum_{m<n}\sum_{\gamma}\frac{A_{m'\gamma';m\gamma,n\gamma}{}^{0(1,2)}A_{n'\delta';m\gamma,n\gamma}{}^{0(1,2)*}}{\epsilon_m+\epsilon_n-2\epsilon_\gamma-\omega(\lambda 0)}$$
$$+\sum_{m}\sum_{\gamma<\delta}\frac{A_{m'\gamma';m\gamma,m\delta}{}^{0(1,2)}A_{n'\delta';m\gamma,m\delta}{}^{0(1,2)*}}{2\epsilon_m-\epsilon_\gamma-\epsilon_\delta-\omega(\lambda 0)}+\sum_{m<n}\sum_{\gamma<\delta}\frac{A_{m'\gamma',(m\gamma,n\delta)_1}{}^{0(1,2)}A_{n'\delta';(m\gamma,n\delta)_1}{}^{0(1,2)*}+A_{m'\gamma';(m\gamma,n\delta)_2}{}^{0(1,2)}A_{n'\delta';(m\gamma,n\delta)_2}{}^{0(1,2)*}}{\epsilon_m+\epsilon_n-\epsilon_\gamma-\epsilon_\delta-\omega(\lambda 0)} \qquad (46)$$

for singlet states and

$$\{\Delta_a(\lambda 1)\}_{m'\gamma',n'\delta'}=\sum_{m<n}\sum_{\gamma}\frac{A_{m'\gamma';(m\gamma,n\gamma)_1}{}^{0(1,2)}A_{n'\delta',(m\gamma,n\gamma)_1}{}^{0(1,2)*}}{\epsilon_m+\epsilon_n-2\epsilon_\gamma-\omega(\lambda 1)}+\sum_{m}\sum_{\gamma<\delta}\frac{A_{m'\gamma';(m\gamma,m\delta)_2}{}^{0(1,2)}A_{n'\delta';(m\gamma,m\delta)_2}{}^{0(1,2)*}}{2\epsilon_m-\epsilon_\gamma-\epsilon_\delta-\omega(\lambda 1)}$$
$$+\sum_{m<n}\sum_{\gamma<\delta}\frac{A_{m'\gamma';(m\gamma,n\delta)_1}{}^{0(1,2)}A_{n'\delta';(m\gamma,n\delta)_1}{}^{0(1,2)*}A_{m'\gamma';(m\gamma,n\delta)_2}{}^{0(1,2)}A_{n'\delta';(m\gamma,n\delta)_2}{}^{0(1,2)*}+A_{m'\gamma';(m\gamma,n\delta)_3}{}^{0(1,2)}A_{n'\delta';(m\gamma,n\delta)_3}{}^{0(1,2)}}{\epsilon_m+\epsilon_n-\epsilon_\gamma-\epsilon_\delta-\omega(\lambda 1)} \qquad (47)$$

for triplet states. To obtain the matrix elements of $\Delta_d(\lambda S)$ one replaces $-\omega(\lambda S)$ by $+\omega(\lambda S)$ in Eqs. (46) and (47). In this approximation the matrices Δ_a and Δ_d are no longer equal and hence $\mathfrak{A}_1$ and $\mathfrak{A}_2$ are not the same. The matrix equation, Eq. (41), will not have the symmetry of the original $1p$–$1h$ theory, Eq. (21). The simplest way around this difficulty is to treat that part of the matrix containing the effects of $2p$–$2h$ states as a perturbation on the $1p$–$1h$ theory. We then have for the excitation frequency, ω,

$$\omega=\omega^{(1p-1h)}-\Delta\omega, \tag{48}$$

with $\Delta\omega$ given by perturbation theory

$$\Delta\omega\simeq\tilde{Y}^*\Delta_a Y+\tilde{Z}^*\Delta_d{}^*Z+{}_bZ+Z^*\Delta_b{}^*Y. \tag{49}$$

Y and Z are the amplitudes obtained in the $1p$–$1h$ approximation and Δ_a, Δ_b, and Δ_d are evaluated using the corresponding frequency. With the approximation equation (44), Eq. (49) reduces to

$$\Delta\omega\simeq\tilde{Y}^*\Delta_a\tilde{Y}+\tilde{Z}^*\Delta_d{}^*Z. \tag{50}$$

Also Z is much smaller than Y and Δ_d is also small compared to Δ_a and hence we neglect the second term on the right hand side of Eq. (50) and use the Y amplitudes of the TDA. This is just the energy lowering of the excited state due to double excitations.

V. CONCLUSIONS

We have discussed the equations-of-motion method as an approach to calculating excitation energies and transition matrix elements of excited states directly as opposed to the conventional approach of obtaining the total energies and wavefunctions of the stationary states of the total Hamiltonian. We have extended our proposed solution of Rowe's variational form of the equation of motion[1]—referred to as a higher random phase approximation[4]—in two ways. First we include the proper renormalization of the equations with respect to the ground state particle–hole densities. These equations now contain renormalized matrix elements but have the same matrix form as the RPA. We have shown that the corrections to the transition energies due to this renormalization are small.[13]

We have also shown how to include the effects of two-particle–hole contributions in the excited states. The single-particle–hole amplitudes are by far the most important in the excitation operator but doubly excited configurations can affect the excitation energies by as much as 2–3 eV. An important conclusion of this section is that the theory with single- and two-particle–hole states can be shown to be equivalent to a single particle–hole theory with a renormalized interaction. Some of these conclusions have been obtained previously using either the quasiboson approximations or time-dependent variational methods.[15] Our approach on the other hand, starts from Rowe's equations,[1] enabling us to derive more general equations, Eq. (41).

We have applied the theory developed in this paper and in Ref. 4 extensively to the excited states of nitrogen, carbon monoxide, ethylene, and benzene. A comparison of the calculated results for N_2 and CO with experiment shows that the theory can predict excitation energies and transition moments accurately and economically.[13]

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[9] This renormalization due to two particle–hole states and the corrections to the RPA included in the theory of Ref. 4 show that one has to be careful in interpreting semiempirical calculations with the RPA.

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[15] See Ref. 1 for references other than Ref. 8.